CARBONATION OF METAL SILICATES FOR
LONG-TERM CO_2 SEQUESTRATION

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RESEARCH OR DEVELOPMENT

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. provisional application serial number 60/464,728, filed April 23, 2003.

BACKGROUND OF THE INVENTION

Rising levels of carbon dioxide (CO_2) in the Earth's atmosphere, caused primarily by combustion of fossil fuels, have prompted concern that temperatures at the Earth's surface will increase sharply during the 21st century. To address this issue, numerous nations are developing plans for lowering CO_2 emissions to the atmosphere. The principal approaches under consideration are: improving energy efficiency; making greater use of alternative sources of energy; and developing economically viable technologies for capture, separation, and long-term storage of CO_2. The latter strategy, known as "CO_2 sequestration," is receiving increasing attention because it permits continued use of high-carbon fossil fuels to generate electrical power while ensuring that CO_2 releases to the atmosphere are reduced.

A potentially attractive means for CO_2 sequestration is injection of gaseous CO_2 into underground reservoirs, e.g., active or depleted oil and gas fields, deep brine formations, and subterranean coalbeds. The underlying premise of this approach is
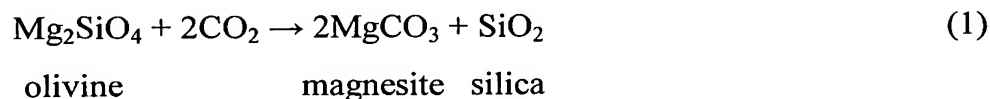
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that, after injection, the CO_2 will remain sequestered in the host rock for hundreds, perhaps even thousands, of years. In practice, however, such long-term reservoir integrity cannot be guaranteed. If either gaseous CO_2 or CO_2-saturated formation water escapes to overlying strata or to the surface, underground and subaerial water

5 supplies could become seriously contaminated, and/or large amounts of CO_2 could be released to the atmosphere.

Significantly, the reservoir-integrity problems associated with subterranean sequestration of gaseous or liquid CO_2 can be completely avoided by chemically binding CO_2 with suitable solid materials. This alternative CO_2 sequestration strategy,

10 known as "mineral carbonation," involves reaction of CO_2 with naturally occurring silicates to produce solid carbonate compounds, such as calcite ($CaCO_3$) and magnesite ($MgCO_3$), for the purpose of long-term terrestrial isolation of CO_2. "Mineral carbonation" also implies a chemical process carried out at elevated temperatures and pressures in an industrial-scale reactor, because a similar term,

15 "mineral trapping," alludes to crystallization of carbonate compounds at ambient temperature and pressure after CO_2 is injected into a subsurface geologic formation. The U.S. Department of Energy (DOE) classifies mineral carbonation as a "CO_2 conversion" technology, rather than a geological CO_2-sequestration strategy, because in mineral carbonation most, if not all, of the CO_2 is converted to one or more solid

20 carbonate compounds, whereas in mineral trapping only a tiny fraction (generally less than one volume %) of the injected CO_2 is ultimately incorporated into solid carbonates.
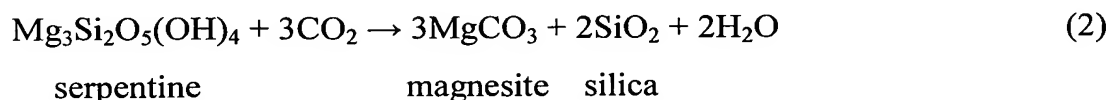
Mineral carbonation has many important advantages over alternative methods for large-scale CO_2 sequestration. First, the carbonate compounds formed in the

25 process are thermodynamically stable, environmentally benign, and weakly soluble in meteoric water. Consequently, they can be amended to soils to reduce acidity and increase moisture content, combined with stone to strengthen roadbeds, or simply dumped in a landfill. Alternatively, the carbonates could be returned to the site of excavation to fill the cavity created by soil/rock removal. Regardless of the particular

30 end use or disposal scheme selected for the carbonates, the reacted CO_2 will remain

2

tightly bound in the crystallographic structures of the carbonates, immobilized for an indefinite period of time. Therefore, a commercial mineral carbonation technology creates no major "legacy issues" for nearby population centers. In contrast, other proposed methods for wide-scale CO_2 sequestration, such as subsurface storage in brine formations, and disposal in deep-ocean realms, rely on risky environmental factors to ensure long-term CO_2 containment: an impervious, superjacent "caprock" in the case of subsurface injection of CO_2 into brine formations, and low ambient temperature and high ambient pressure, with no current-driven dispersal of the sequestration "agent" (liquid CO_2 or CO_2-hydrate), in the case of suboceanic CO_2 disposal.
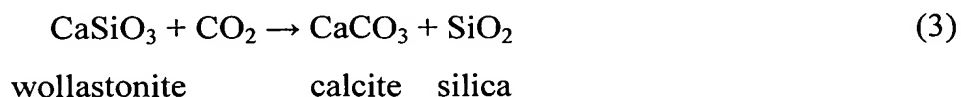
In weighing the technical feasibility of CO_2 sequestration by mineral carbonation, it should be noted that huge masses of rocks and clay-rich formations suitable for carbonation occur worldwide. For example, ultramafic complexes and large serpentinite bodies are major sources of the magnesium-rich minerals olivine (forsterite) and serpentine, which can be carbonated by the reactions
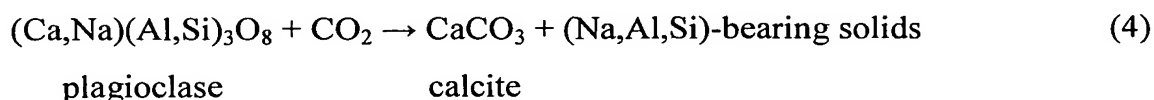
$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \qquad (1)$$
$$\text{olivine} \qquad\qquad\qquad \text{magnesite} \quad \text{silica}$$

and

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \qquad (2)$$
$$\text{serpentine} \qquad\qquad\qquad \text{magnesite} \quad \text{silica}$$

Moreover, contact-metamorphosed limestones frequently contain wollastonite ($CaSiO_3$), and large quantities of plagioclase [$(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x})O_8$] are present in many different types of common rocks. Wollastonite and plagioclase can be converted to calcite (plus silicious solid material) by the reactions

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \qquad (3)$$
$$\text{wollastonite} \qquad\qquad \text{calcite} \quad \text{silica}$$

and

$$(Ca,Na)(Al,Si)_3O_8 + CO_2 \rightarrow CaCO_3 + (Na,Al,Si)\text{-bearing solids} \qquad (4)$$
$$\text{plagioclase} \qquad\qquad\qquad \text{calcite}$$

3

Another key attribute of mineral carbonation, in relation to other technologies that deal with CO_2 waste streams, is that costs associated with CO_2 transport are potentially very low. This is so because in an industrial-scale implementation of a mineral carbonation technology, the metal-silicate feedstock can be carbonated in commercial facilities located adjacent to, or near, large "point sources" of CO_2 generation, such as fossil fuel-fired power plants, cement factories, and steel mills. In contrast, CO_2 sequestration in deep brine aquifers, or the benthic regions of the world's major oceans, would often require CO_2 transport over substantial distances. Building and maintaining many miles of pipeline to achieve such transport, or hauling liquid CO_2 over long distances by truck, train or ship, would be extremely expensive and perhaps totally impractical.

Finally, the following additional advantages of mineral carbonation are noteworthy: (1) by technical necessity, mineral carbonation involves rapid conversion of CO_2 to solid carbonate(s), and (2) by virtue of creating one or more solid carbonate phases from a volatile phase rich in CO_2, carbonate crystallization automatically produces a large reduction in total volume. It has already been demonstrated by researchers at the Albany Research Center in Oregon, and the Los Alamos National Laboratory in New Mexico, that, with vigorous mechanical stirring, olivine and heat-pretreated serpentine can be quantitatively converted to magnesite (see Reactions 1 and 2 above) in ~30 minutes at 155°C and 185 atm total (fluid) pressure. Significantly, the latter processing conditions are readily attained in modern industrial reactors. A large reduction in the total volume of the reactants (CO_2, plus one or more condensed phases, and often one or more "additives" and/or catalysts) is automatically achieved in mineral carbonation because the CO_2-bearing solids produced are >1000x more dense than gaseous CO_2 at STP (standard temperature and pressure: 25°C, 1 atm). This contraction essentially eliminates the "room problem" associated with storing large volumes of CO_2 (as a gas, liquid or supercritical fluid) in subsurface rock formations.

While it is evident that mineral carbonation offers many important advantages over competing CO_2 sequestration technologies, it is also true that it suffers two major

4

disadvantages. Chief among these is the need to mine, or quarry, large quantities of silicate feedstock to sequester the gigatons of atmospheric CO_2 generated annually by combustion of fossil fuels. Excavating massive amounts of rock and soil to permit silicate carbonation at sites near major industrial sources of CO_2 will be expensive,

5 and will require intense reclamation activities to restore the land to an environmentally acceptable state. However, there is no doubt that this can be accomplished using modern methods of environmental restoration. In addition, it is likely that new technologies will soon be developed to enable innovative synergies, and more satisfactory compromises, between large-scale energy production and traditional

10 modes of land use.

The second major disadvantage of mineral carbonation is that elevated temperatures and pressures, and chemical "additives" and/or catalysts, are usually required to accelerate CO_2 conversion to one or more crystalline carbonates. While considerable success has already been achieved in carbonating olivine (Reaction 1) at

15 commercially feasible temperatures and pressures, mineral carbonation experiments performed over the past four years at the Albany Research Center have shown that untreated serpentine does not react as readily (Reaction 2). To date, the only known remedy for sluggish serpentine carbonation is to heat-pretreat the mineral to 600-650°C prior to carbonation, which drives off structurally bound water (hydroxyl

20 groups). Tests of this altered (dehydroxylated) serpentine have shown that it is much more reactive than untreated (hydroxylated) serpentine. However, at a typical fossil fuel-fired power plant, heat treating serpentine at 600-650°C prior to carbonation would require ~200 kW·hr of electricity per ton of serpentine feedstock. With one ton of carbon in a fossil fuel producing ~3.7 tons of CO_2, and each ton of CO_2 consuming

25 ~2.0 tons of serpentine during carbonation, the power requirements for serpentine dehydroxylation represent 20-30% of total power output. This large energy penalty threatens the economic viability of CO_2 sequestration by serpentine carbonation.

It is evident from Reactions 3 and 4 that the problems plaguing serpentine carbonation would be partly or entirely avoided if a more abundant silicate mineral could be utilized. In this regard, it is noteworthy that wollastonite is carbonated by

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Reaction 3 at 60°C using an aqueous solution of acetic acid as a catalyst. This result is of some scientific interest, but it fails to significantly bolster metal-silicate carbonation as a potential means for sequestering large masses of CO_2 because wollastonite, while not rare in nature, is typically found in significant quantities only in contact

5   metamorphic aureoles where it tends, along with other silicates, to form small, isolated bodies adjacent to igneous intrusions. The other principal occurrence of wollastonite is as a widely disseminated mineral in regionally metamorphosed carbonate strata. Thus, wollastonite is not available in sufficient quantities to sustain a wide-scale silicate carbonation technology.

10   The low abundance of wollastonite leaves plagioclase as the major potential source of calcium (Reaction 4) to produce the quantities of carbonate required to sequester gigatons of CO_2 by metal-silicate carbonation. (Other, *locally* significant potential sources of calcium include Ca-rich clay deposits, Ca-rich fly ash, and waste concrete.) However, a commercially feasible plagioclase carbonation technology faces

15   two formidable technical challenges. First, it is inherently difficult to extract calcium from plagioclase because, being a framework silicate with a three-dimensional structure held together by tightly bonded atoms of silicon and aluminum, plagioclase is not readily destabilized by firing at high temperatures, or easily "digested" (decomposed) by most customary solvents. Second, while most plagioclases contain a

20   significant amount of calcium, Ca-contents are always less than that of wollastonite. Therefore, per ton of silicate feedstock, less calcium-rich carbonate (calcite) is formed from plagioclase than from wollastonite. These difficulties notwithstanding, it is clear that plagioclase carbonation merits serious scientific study to determine whether it could be an attractive alternative to serpentine carbonation in sequestering large

25   quantities of CO_2.

SUMMARY OF THE INVENTION

In a preferred embodiment, the invention relates to a process of sequestering carbon dioxide. The process comprises the steps of: (a) reacting a metal silicate with a caustic alkali-metal hydroxide to produce a hydroxide of the metal formerly

30   contained in the silicate; (b) reacting carbon dioxide with at least one of a caustic

6

alkali-metal hydroxide and an alkali-metal silicate to produce at least one of an alkali-metal carbonate and an alkali-metal bicarbonate; and (c) reacting the metal hydroxide product of step (a) with at least one of the alkali-metal carbonate and the alkali-metal bicarbonate produced in step (b) to produce a carbonate of the metal formerly contained in the metal silicate of step (a).

The invention also relates to a system for sequestering carbon dioxide from a gas stream. The system comprises a gas stream containing carbon dioxide, a first reaction chamber for reacting a metal silicate with a caustic material to produce a hydroxide of the metal, and a second reaction chamber for contacting the metal hydroxide with the gas stream containing the carbon dioxide to produce a carbonate of the metal.

The invention also relates to a system for carbonating a metal silicate. The system comprises: (a) a supply of the metal silicate entering the system; (b) a source of carbon dioxide entering the system; (c) a reactor structured for converting the metal silicate to a metal carbonate and silica with the use of a caustic material, and with the use of the carbon dioxide; and (d) the metal carbonate and the silica exiting the system as separate products.

The invention also relates to a system for recovering a useful metal from rock. The system comprises: (a) a supply of rock entering the system, the rock containing the useful metal and a metal silicate; (b) a source of carbon dioxide entering the system; (c) a reactor structured for converting the metal silicate to a metal carbonate, with the use of a caustic material, and with the use of the carbon dioxide; (d) apparatus for removing the useful metal from the rock; (e) a stream of the metal carbonate exiting the system; and (f) a stream of the useful metal exiting the system.

The invention also relates to a process of carbonating a metal silicate. The process comprises the steps of: (a) reacting the metal silicate with a caustic material to produce a hydroxide of the metal; (b) reacting the metal hydroxide with a source of carbon dioxide to produce a carbonate of the metal and to produce reconstituted caustic material; and (c) introducing the caustic material from step (b) into step (a).

7

The invention also relates to a process of carbonating a metal silicate. The process comprises reacting at least the metal silicate and a source of carbon dioxide to produce a carbonate of the metal, wherein the reaction is conducted at a pressure not greater than about 50 bars above the vapor pressure of pure water for the temperature of the reaction.

The invention also relates to a process of carbonating a metal silicate. The process comprises the steps of: (a) reacting the metal silicate with a caustic alkali-metal hydroxide to produce a hydroxide of the metal formerly contained in the silicate; and (b) reacting the metal hydroxide with a source of carbon dioxide to produce a carbonate of the metal formerly contained in the metal silicate of step (a).

The invention also relates to a process of producing a metal carbonate. The process comprises reacting an alkaline-earth metal hydroxide with at least one of an alkali-metal carbonate, an alkali-metal bicarbonate, and carbon dioxide, to produce a carbonate of the metal formerly contained in the metal hydroxide.

The following detailed discussion will make the advantages of the invention apparent to the informed reader.

DETAILED DESCRIPTION OF THE INVENTION

Many different types of metal-silicate feedstocks are amenable to carbonation by the invented process, including naturally occurring silicates such as those present in rocks and clay-rich formations, as well as silicates present in industrial waste products such as fly ash and waste concrete. Typically, the metal-silicate feedstock is composed of one or more calcium silicates, magnesium silicates, iron-bearing silicates (such as basalt), or mixtures thereof, although other types of silicates can also be used. Some nonlimiting examples of these silicates are described below. (Silicate feedstocks are referred to collectively herein as "metal silicates" with the understanding that this designation includes any natural or man-made material, in the crystalline or amorphous state, that contains at least one metal along with silicon. By this definition, aluminosilicates are metal silicates because they contain a metal, aluminum, along with silicon.)

Calcium silicates include wollastonite ($CaSiO_3$), calcic plagioclase [e.g.,
anorthite [$(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x}O_8$, where $x \geq 0.9$, and labradorite
[$(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x}O_8$, where $0.5 \leq x \leq 0.7$], calcium-rich fly ash, basalt (a volcanic
rock rich in Ca, Mg and Fe), calcium-rich montmorillonite [nominally

5   ($\frac{1}{2}$Ca,Na)$_{0.7}$(Al,Mg,Fe)$_4$[(Si,Al)$_8$O$_{20}$] (OH)$_4 \cdot$nH$_2$O] and waste concrete. Contact-
metamorphosed limestones frequently contain wollastonite, large quantities of calcic
plagioclase are present in many different types of common rocks, and calcium-rich
montmorillonite is found in special types of clay deposits. Basalt is a common rock in
many terrestrial locations, and on the floors of the world's major oceans.

10   Magnesium-rich silicates include olivine (specifically forsterite, Mg_2SiO_4),
serpentine [$Mg_3Si_2O_5(OH)_4$], and basalt. Significant masses of olivine- and
serpentine-bearing rocks exist around the world, particularly in ultramafic complexes,
and in large serpentinite bodies.

Iron-bearing silicates include fayalite, Fe_2SiO_4, and various natural glasses

15   (e.g., basaltic glass).

The metal silicates used as feedstocks for the process can have a wide range of
initial particle sizes. Typically, it is desirable to reduce the particle size of the metal
silicate(s) prior to chemical treatment. For example, the particle size of the metal
silicate(s) may be reduced to an average diameter of less than about 100 microns. Any

20   suitable equipment can be used to reduce particle size.

The process can optionally be conducted without heat pretreatment of the metal
silicate feedstock.

In a preferred embodiment of the invention, one or more metal silicates are
transformed to one or more solid hydroxides by reaction with a caustic alkali-metal

25   hydroxide, such as caustic soda (NaOH), in aqueous solution. This is the first step of a
preferred process; i.e., the metal silicate(s) react with a caustic alkali-metal hydroxide
to produce a hydroxide of the metal formerly contained in the silicate. This initial
reaction is usually followed by physical and chemical segregation of the produced
solid(s) and "depleted" caustic liquid. In addition, it may be desirable to separate the

9

solid metal hydroxide(s) from any residual solid silicate and/or oxide material that forms as a byproduct of caustic digestion.

Any suitable concentration of the caustic alkali-metal hydroxide in aqueous solution can be used to decompose the metal-silicate feedstock, including highly concentrated and very dilute solutions. The caustic solution is typically fairly concentrated, comprising, by weight, from about 30% to about 80% NaOH and from about 20% to about 70% water.

In the final step of the preferred process, the metal hydroxide formed in the first step is reacted with alkali-metal carbonate (e.g., sodium carbonate) and/or alkali-metal bicarbonate (e.g., sodium bicarbonate) to produce a carbonate of the metal formerly contained in the metal silicate. This reaction can be induced at any suitable set of temperature-pressure conditions.

An intermediate step in the preferred process involves reacting carbon dioxide with caustic alkali-metal hydroxide (e.g., NaOH) and/or alkali metal silicate (e.g., Na_2SiO_3) to produce alkali-metal carbonate (e.g., Na_2CO_3) and/or alkali-metal bicarbonate (e.g., $NaHCO_3$), ± water and/or silica in either gelatinous or solid form. This step may or may not be followed by precipitation of the Na_2CO_3 and/or $NaHCO_3$, which could be achieved by shifting the pH of the aqueous solution, or by evaporating off some of the water present.

When all of the foregoing steps are carried out using straight flue gas as a source of CO_2, capture, separation and sequestration of that gas is achieved in a single, integrated operation.

Advantageously, the caustic material produced in the intermediate step of the process can usually be recycled back into the first step of the process. Thus, more generally, the invention relates to a process of carbonating a metal silicate which comprises the steps of: (a) reacting the metal silicate with a caustic material to produce a hydroxide of the metal; (b) reacting the metal hydroxide with a source of carbon dioxide to produce a carbonate of the metal and to produce reconstituted caustic material; and (c) introducing the caustic material from step (b) into step (a).

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The caustic material can be a caustic alkali-metal hydroxide or any other suitable caustic material.

It has been discovered by the inventors that the intermediate and final steps of the process can be conducted at a pressure not greater than about 50 bars above the vapor pressure of pure water for the temperature of these two steps, typically not greater than about 30 bars, and more typically not greater than about 20 bars, and often not greater than about 10 bars. The initial step can be conducted at a pressure slightly below the vapor pressure of pure water for the temperature of that step. Achieving rapid chemical reaction at low pressure is a key technological advantage because relatively thin-walled pressure chambers will suffice to safely contain the aqueous liquids (± gas) as reaction proceeds. This will reduce the costs of commercial reactors built to implement the process on an industrial scale. Moreover, when total pressure is equal to the vapor pressure of the liquid phase, no investments in expensive pressure-intensifying equipment are required. On the other hand, higher fluid (liquid and/or gas) pressures at each step, particularly the intermediate step, could lead to more rapid and efficient chemical reaction, in which case additional capital expenditures to make the carbonation reactor more structurally robust, and to procure suitable pumping equipment, might be cost effective.

More generally, the invention relates to a process of carbonating a metal silicate. The process comprises reacting at least the metal silicate and a source of carbon dioxide to produce a carbonate of the metal, wherein the reaction is conducted at a pressure not greater than about 50 bars above the vapor pressure of pure water for the temperature of the reaction.
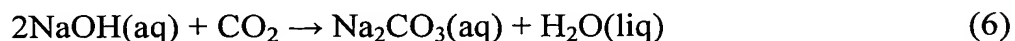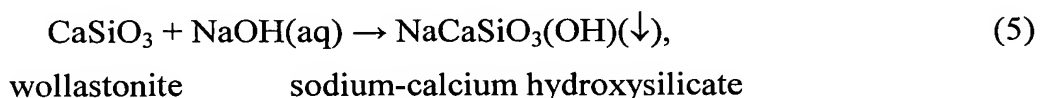
However, it may be beneficial to pressurize the CO_2-bearing gas to a level above the vapor pressure of pure water for the temperature of the step in which it is reacted, prior to, or during, production of metal carbonate(s) and/or metal bicarbonate(s) in order to accelerate rates of carbonation. If CO_2 is captured, separated and liquified by a another process, then pressures up to ~64 atm (the vapor pressure of pure liquid CO_2 at 25°C) could be achieved simply by throttling flow of CO_2 into the pressure chamber used to achieve carbonation.

11

In each step of the preferred process, the extent to which aqueous liquids are agitated or stirred, and control of the proportions of phases as reaction proceeds, can be varied. In general, chemical reaction is accelerated by vigorously agitating or rapidly stirring the reactants as processing proceeds, and by maintaining high fluid
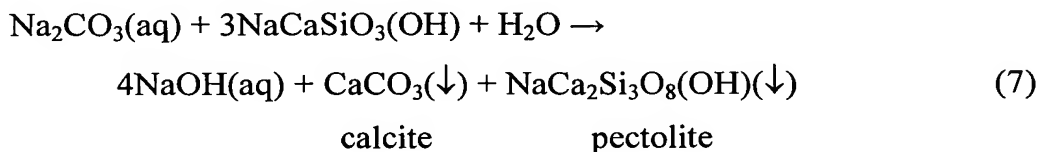
5   /solid ratios.

More generally, the invention relates to a process of carbonating a metal silicate which comprises the steps of: (a) reacting the metal silicate with a caustic alkali-metal hydroxide to produce a hydroxide of the metal formerly contained in the silicate; and (b) reacting the metal hydroxide with a source of carbon dioxide to

10   produce a carbonate of the metal formerly contained in the metal silicate of step (a). The invention also relates to a process of producing a metal carbonate. This process comprises reacting an alkaline-earth metal hydroxide with at least one of an alkali-metal carbonate, an alkali-metal bicarbonate, and carbon dioxide, to produce a carbonate of the metal formerly contained in the metal hydroxide.

15   Some examples of reaction pathways for carbonating particular kinds of metal silicates are described below. It should be recognized that the invention is not limited to these specific examples.
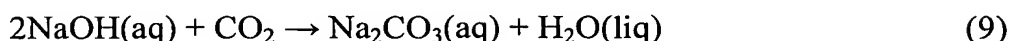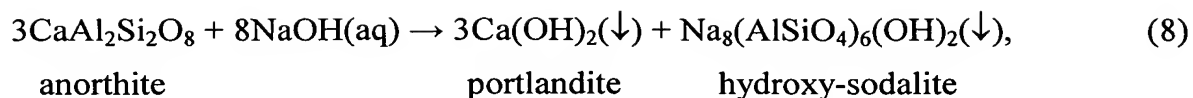
The invented process is advantageously used to carbonate calcium silicates. For wollastonite (nominally $CaSiO_3$), the processing reactions are:
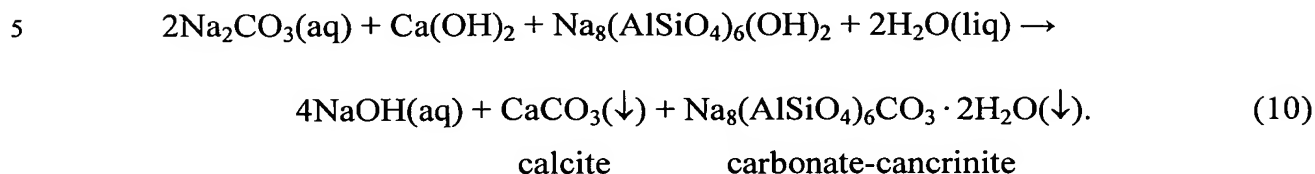
20    $$CaSiO_3 + NaOH(aq) \rightarrow NaCaSiO_3(OH)(\downarrow), \qquad (5)$$
wollastonite   sodium-calcium hydroxysilicate

$$2NaOH(aq) + CO_2 \rightarrow Na_2CO_3(aq) + H_2O(liq) \qquad (6)$$

and

$$Na_2CO_3(aq) + 3NaCaSiO_3(OH) + H_2O \rightarrow$$

25    $$4NaOH(aq) + CaCO_3(\downarrow) + NaCa_2Si_3O_8(OH)(\downarrow) \qquad (7)$$
calcite   pectolite

(aq = aqueous, $\downarrow$ = precipitate, liq = liquid), respectively. For anorthite ($CaAl_2Si_2O_8$), the processing reactions are:
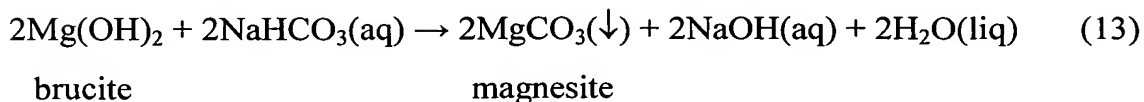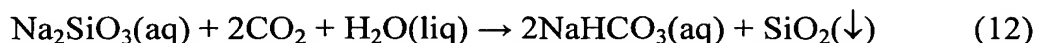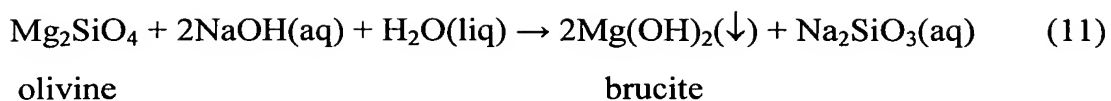
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$$3CaAl_2Si_2O_8 + 8NaOH(aq) \rightarrow 3Ca(OH)_2(\downarrow) + Na_8(AlSiO_4)_6(OH)_2(\downarrow), \qquad (8)$$

    anorthite   portlandite   hydroxy-sodalite

$$2NaOH(aq) + CO_2 \rightarrow Na_2CO_3(aq) + H_2O(liq) \qquad (9)$$

and

$$2Na_2CO_3(aq) + Ca(OH)_2 + Na_8(AlSiO_4)_6(OH)_2 + 2H_2O(liq) \rightarrow$$

$$4NaOH(aq) + CaCO_3(\downarrow) + Na_8(AlSiO_4)_6CO_3 \cdot 2H_2O(\downarrow). \qquad (10)$$

                    calcite   carbonate-cancrinite
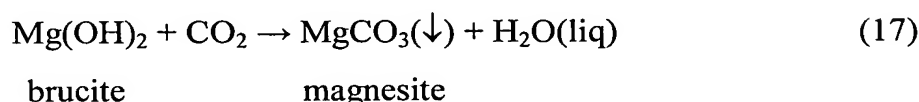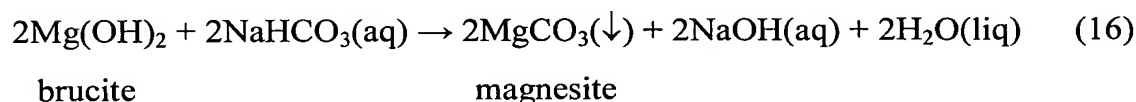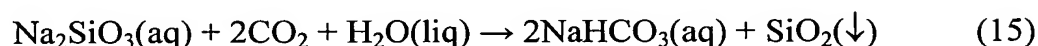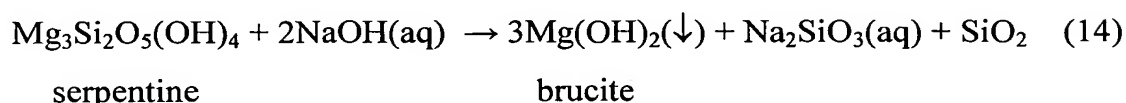
(Other Ca-rich aluminosilicates carbonate by reactions similar to those for anorthite, with concomitant formation of various kinds of residual solid materials.) The NaOH "regenerated" in the third step of the process (e.g., Reactions 7 and 10) can be recycled to decompose additional calcium silicate in step 1 (e.g., Reactions 5 and 8), or to form additional Na_2CO_3 in step 2 (e.g., Reactions 6 and 9). Table 1 presents the results of experiments, performed by the inventors, that confirm Reactions 5-10.

In step 1 of the calcium-silicate carbonation processes (e.g., Reactions 5 and 8), a solid, calcium-rich silicate feedstock is decomposed in an aqueous solution of caustic soda to produce crystalline sodium-calcium hydroxysilicate, or crystalline portlandite and crystalline hydroxy-sodalite. This step is followed by physical and chemical segregation of the precipitated solid(s) and "depleted" caustic liquid. In step 2 (e.g., Reactions 6 and 9), carbon dioxide is injected into a NaOH-bearing aqueous liquid, creating aqueous Na_2CO_3 and water. In step 3 (e.g., Reactions 7 and 10), the Na_2CO_3 generated in step 2 is reacted with the crystalline hydroxide(s) formed in step 1 to produce aqueous NaOH, and either crystalline calcite + crystalline pectolite, or crystalline calcite + crystalline carbonate-cancrinite. These solid reaction products are thermodynamically stable, environmentally benign, and sparingly soluble in meteoric water.

The invented process also converts magnesium-rich silicates to magnesium-rich carbonates. For example, the following process reactions produce magnesite ($MgCO_3$) from the magnesium-rich minerals olivine (specifically forsterite, Mg_2SiO_4) and serpentine [$Mg_3Si_2O_5(OH)_4$]:

$$Mg_2SiO_4 + 2NaOH(aq) + H_2O(liq) \rightarrow 2Mg(OH)_2(\downarrow) + Na_2SiO_3(aq) \qquad (11)$$
olivine   brucite

$$Na_2SiO_3(aq) + 2CO_2 + H_2O(liq) \rightarrow 2NaHCO_3(aq) + SiO_2(\downarrow) \qquad (12)$$

$$2Mg(OH)_2 + 2NaHCO_3(aq) \rightarrow 2MgCO_3(\downarrow) + 2NaOH(aq) + 2H_2O(liq) \qquad (13)$$
brucite   magnesite

[Net reaction: $Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3(\downarrow) + SiO_2(\downarrow)$], and

$$Mg_3Si_2O_5(OH)_4 + 2NaOH(aq) \rightarrow 3Mg(OH)_2(\downarrow) + Na_2SiO_3(aq) + SiO_2 \qquad (14)$$
serpentine   brucite

$$Na_2SiO_3(aq) + 2CO_2 + H_2O(liq) \rightarrow 2NaHCO_3(aq) + SiO_2(\downarrow) \qquad (15)$$

$$2Mg(OH)_2 + 2NaHCO_3(aq) \rightarrow 2MgCO_3(\downarrow) + 2NaOH(aq) + 2H_2O(liq) \qquad (16)$$
brucite   magnesite

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3(\downarrow) + H_2O(liq) \qquad (17)$$
brucite   magnesite

[Net reaction: $Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3(\downarrow) + 2SiO_2(\downarrow) + 2H_2O(liq)$]. Table 2 presents the results of experiments, performed by the writers, that confirm Reactions 11-17.

A key observation concerning Reaction 14 is that no heat pretreatment of the serpentine is required to achieve rapid and efficient production of $Mg(OH)_2$. This contrasts sharply with the so-called "direct" method for carbonating serpentine (by the reaction $Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$), which requires heat pretreatment of the serpentine at ~600°C to drive off structurally bound water. This extra step is necessary in the direct method of carbonating serpentine because water-bearing (hydroxylated) serpentine reacts sluggishly with CO_2, whereas dewatered (dehydroxylated) serpentine is highly reactive. Dehydroxylation of serpentine makes the direct carbonation method very energy intensive and costly. In this regard, it is also noteworthy that the invented process, as applied to either olivine or serpentine, completely conserves the "rock solvent" (e.g., NaOH), which lowers overall processing costs. By contrast, in the direct method for carbonating serpentine and

14

olivine, the rock solvent is (effectively) compressed, supercritical CO_2, which is expensive to create due to the high capital and operating costs of the mechanical pumping that is required to achieve pressures as high as 185 atm.
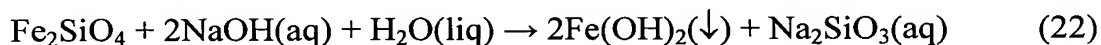
Another important discovery made by the inventors is that $Mg(OH)_2$ can be reacted with Na_2CO_3 at 200°C and elevated CO_2 fugacities to form the double carbonate eitelite $[Na_2Mg(CO_3)_2]$ (see Table 2), which contains twice as much CO_2 as magnesite $(MgCO_3)$. Crystallization of eitelite would permit twice as much CO_2 to be sequestered per ton of mined Mg-rich rock. In addition, like magnesite, eitelite is thermodynamically stable, environmentally neutral, and only weakly soluble in meteoric water. However, a disadvantage of eitelite crystallization is that caustic soda is not "regenerated" simultaneously, as it is when magnesite crystallizes (see Reactions 13 and 16). Therefore, when either olivine or serpentine is used to produce eitelite, the cost-savings achieved by reducing the tonnage of mined Mg-rich rock are offset to a significant extent by the continuous need to replenish the supply of NaOH that is used to decompose the metal-silicate feedstock.

It should be clearly understood that the chemical formulae for the solutes (substances dissolved in aqueous solution) in Reactions 11-13 and 14-16 (specifically NaOH, Na_2SiO_3 and $NaHCO_3$) represent stoichiometric components in aqueous solution, *not* "real" aqueous species. This convention was adopted (see also Reactions 5-7 and 8-10) for the sake of generality and simplicity. The particular species in aqueous solution created by our process (presently unknown) are of considerable scientific interest; however, they need not be represented explicitly in sets of process reactions such as those above, because the *solids* that form and disappear in each process reaction, as well as the *net* carbonation reaction for each metal silicate, do not depend on the chemical formulae that are used to represent the compositions of solutes. A simple example serves to illustrate this point. In Reactions 11-13, the stoichiometric components NaOH, Na_2SiO_3 and $NaHCO_3$ can be replaced by the ionic species OH^-, $SiO(OH)_3^-$, and HCO_3^-, with sodium ion omitted because it is neither consumed nor produced in any reaction. This leads to the following alternative carbonation pathway for forsteritic olivine:
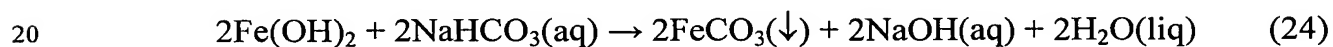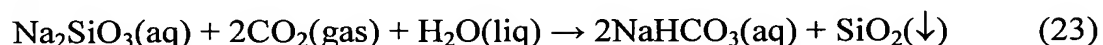
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$$Mg_2SiO_4 + OH^- + 3H_2O \rightarrow 2Mg(OH)_2 + SiO(OH)_3^- \qquad (18)$$

$$SiO(OH)_3^- + CO_2 \rightarrow HCO_3^- + SiO_2(\downarrow) + H_2O \qquad (19)$$

$$Mg(OH)_2 + HCO_3^- \rightarrow MgCO_3(\downarrow) + OH^- + H_2O \qquad (20)$$

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3(\downarrow) + H_2O \qquad (21)$$
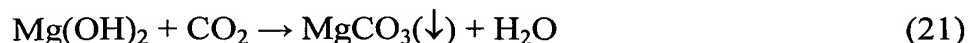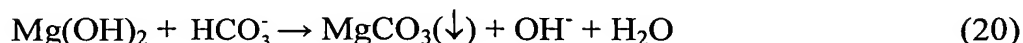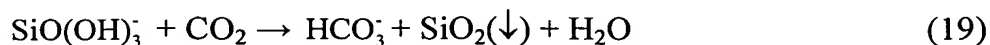
[Net reaction: $Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3(\downarrow) + SiO_2(\downarrow)$]. Comparing Reactions 18-21 with Reactions 11-13, it is evident that the solids consumed and produced, and the net reaction, are identical. Therefore, it should be clearly understood that the scope of our process for carbonating metal silicates includes various self-consistent sets of reactions—i.e., sets of reactions involving the same solids, with metal silicate digestion by one or more caustic metal hydroxides (such as NaOH)—wherein solutes are represented by aqueous species of varying composition and charge, rather than by stoichiometric components.

The invented process may also convert iron-bearing silicates to iron-bearing carbonates, following carbonation pathways similar to those described above for Ca- and Mg-rich silicates. This is illustrated below for the iron-bearing silicate fayalite, Fe_2SiO_4:

$$Fe_2SiO_4 + 2NaOH(aq) + H_2O(liq) \rightarrow 2Fe(OH)_2(\downarrow) + Na_2SiO_3(aq) \qquad (22)$$
fayalite

$$Na_2SiO_3(aq) + 2CO_2(gas) + H_2O(liq) \rightarrow 2NaHCO_3(aq) + SiO_2(\downarrow) \qquad (23)$$

$$2Fe(OH)_2 + 2NaHCO_3(aq) \rightarrow 2FeCO_3(\downarrow) + 2NaOH(aq) + 2H_2O(liq) \qquad (24)$$
siderite

[Net reaction: $Fe_2SiO_4 + 2CO_2 \rightarrow 2FeCO_3(\downarrow) + SiO_2(\downarrow)$]. It is likely that similar reactions will convert Fe-bearing silicate glasses (e.g., basaltic glass) to one or more Fe-bearing carbonates.

In another embodiment of the invention, Ca-rich silicates are carbonated in a single step. In this alternative carbonation pathway, the silicate feedstock, aqueous NaOH, and Na_2CO_3 are reacted to produce crystalline calcite ± crystalline sodium-calcium hydroxysilicate ± crystalline hydroxy-sodalite ± crystalline carbonate-

16

cancrinite ± residual silicate material. For example, using a concentrated aqueous solution of caustic soda (such as 50 weight percent NaOH in H_2O) as the silicate solvent, and by adding abundant sodium carbonate to that solution to serve as a source of CO_2, the aluminum-bearing calcium silicates anorthite and labradorite react with

NaOH and Na_2CO_3 to form crystalline calcite ± crystalline hydroxy-sodalite ± residual aluminosilicate material at 200°C and a total (fluid) pressure <15 atm (see Table 1).

The single-step process for carbonating Ca-rich silicates is simpler than the three-step process described earlier, because physical and chemical segregation of the solids and liquids is not required. However, the one-step process has the disadvantage that carbonate-cancrinite is typically not among the solids that are produced. (In the "one-step" experiments performed by the inventors using Ca-rich silicates as a source of calcium, carbonate-cancrinite was only observed in experiments performed with Ca-rich fly ash.) A plausible explanation for this is that the aqueous fluids produced in one-step experiments were typically too basic to allow carbonate-cancrinite to crystallize. Therefore, in an industrial-scale implementation of the one-step process, it may be desirable, at some point, to lower the pH of the aqueous fluid to increase the possibility that carbonate-cancrinite will be produced. The formation of carbonate-cancrinite significantly increases the total "CO_2-loading" of the solids produced, and therefore leads to more efficient and cost-effective carbonation of the Ca-silicate feedstock.

In still another embodiment, the invention provides a means for carbonating magnesium and iron silicates in two steps. In step 1, the metal silicate(s) is (are) converted to $Mg(OH)_2$ and/or iron hydroxides(s) + Na_2SiO_3 ± SiO_2 by reaction with caustic soda in aqueous solution (e.g., Reactions 11, 14 and 22). When this conversion is essentially complete, carbonation of $Mg(OH)_2$ and/or iron hydroxide(s) is (are) achieved by injecting CO_2 into the aqueous solution to form $NaHCO_3$ (± Na_2CO_3) + silica gel and/or solid silica (step 2). $MgCO_3$ is formed when the $Mg(OH)_2$ produced in step 1 reacts with $NaHCO_3$ (± Na_2CO_3) and/or aqueous CO_2 (e.g., Reactions 13, 16 and 24).

Physical and/or chemical segregation of solids and liquids is not required in the two-step process for carbonating Mg- and Fe-rich silicates; therefore, it is intrinsically simplier than the three-step process for carbonating forsteritic olivine (Reactions 11-13), and the four-step process for carbonating serpentine (Reactions 14-17). On the other hand, the two-step process has the disadvantage that silica and magnesite are produced simultaneously. It should be recognized that Reactions 11-13 and 14-17 produce separate "streams" of gelatinous/solid silica and crystalline magnesite, which allows each substance to be used as a feedstock for various commercial applications. In contrast, the two-step process for carbonating magnesium and iron silicates generates a single stream of solid material, consisting of intimately mixed gelatinous/solid silica and crystalline magnesite. This creates two difficulties. First, gelatinous silica (if formed) is readily mobilized by meteoric water, and is therefore an inherently undesirable waste product for near-surface terrestrial disposal. Second, when silica (in any form) and magnesite are intimately mixed, the high cost of separation effectively precludes any value-added commercial applications of each substance. Therefore, compared to separate masses of its individual components, an intimate mixture of silica and magnesite is an economic and environmental liability.

The invention also relates to a system for sequestering carbon dioxide from a gas stream. The system includes a gas stream containing carbon dioxide, for example, a flue gas containing carbon dioxide or a stream of pure carbon dioxide gas. The system also includes a first reaction chamber for reacting a metal silicate with a caustic material to produce a hydroxide of the metal. The caustic material can be a caustic alkali-metal hydroxide, as discussed above, or any other caustic material suitable for the reaction. The system also includes a second reaction chamber for contacting the metal hydroxide with the gas stream containing the carbon dioxide to produce a carbonate of the metal. The first and second reaction chambers can be located in the same reactor or in different reactors. More than two reaction chambers can optionally be used in the system.

The invention also relates to a system for carbonating a metal silicate. The system includes a supply of the metal silicate entering the system, and a source of

carbon dioxide entering the system. The source of carbon dioxide can be a gas stream containing carbon dioxide, or it can be a compound containing carbon dioxide, such as an alkali-metal carbonate or bicarbonate. The system also includes a reactor structured for converting the metal silicate to a metal carbonate and silica with the use of a

5 caustic material, and with the use of the carbon dioxide. Any suitable caustic material can be used, such as a caustic alkali-metal hydroxide. The reaction can include other reactants in addition to the metal silicate, the caustic material and the carbon dioxide. The metal carbonate and the silica exit the system as separate products. In a preferred embodiment, the metal silicate is magnesium silicate and the metal carbonate is

10 magnesite. Typically, the magnesite and the silica exiting the system have a purity of at least about 90%. This is economically advantageous, and it contrasts with previously known processes that produce mixtures of magnesite and silica.

The invention also relates to a system for recovering a useful metal from rock. The system includes a supply of rock entering the system, the rock containing the

15 useful metal and a metal silicate, and a source of carbon dioxide entering the system. The system also includes a reactor structured for converting the metal silicate to a metal carbonate, with the use of a caustic material, and with the use of the carbon dioxide. As discussed above, any suitable caustic material can be used, and the source of carbon dioxide can be a gas containing carbon dioxide or a compound containing

20 carbon dioxide. The system also includes apparatus for removing the useful metal from the rock. The apparatus can be located at any suitable location in the system. For example, magnetic apparatus can be used for removing magnetite from serpentine prior to the reactor. Alternatively, the reactor can produce the metal carbonate and a remaining rock portion, and the system can include apparatus for removing the useful

25 metal from the remaining rock portion at a location subsequent to the reactor. The system also includes a stream of the metal carbonate exiting the system, and a stream of the useful metal exiting the system. The streams can be in any form, such as truckloads, trainloads, or other means of conveying the metal carbonate and the useful metal from the system.

19

The carbonation pathways for Ca-, Mg- and Fe-rich silicates described above are similar to, but distinctly different from, the commercial chemical processes that are used to extract alumina (Al_2O_3) from bauxite (aluminum ore), and to generate caustic soda from trona (a rock rich in sodium carbonate, Na_2CO_3). In the treatment of

5   bauxite ore by the well-known Bayer Process, caustic soda is used to remove reactive silica and iron oxides, and to dissolve aluminum oxides (gibbsite, boehmite and diaspore). Dissolution of silica by the caustic solution produces sodium silicate (nominally Na_2SiO_3), which quickly reacts with sodium aluminate ($NaAlO_2$) to form crystalline hydroxy-sodalite [$Na_8(AlSiO_4)_6(OH)_2$]. This desilication of the solution is

10 detrimental to the overall process because it consumes caustic soda, and the total mass of dissolved sodium aluminate is lowered. (With less sodium aluminate in solution, less high-purity gibbsite is precipitated in a later stage of the process, and as a second consequence, less caustic soda is regenerated by gibbsite precipitation. Regenerated caustic soda is recycled in the Bayer Process to treat additional batches of bauxite ore.)

15 While the Bayer Process has several characteristics in common with the process described in this document—in particular, the use of caustic soda to decompose the metal-bearing, solid feedstock, and regeneration of caustic soda at a subsequent stage of the process—two major differences are also evident. The first is that the goals of the two processes are totally different: the Bayer Process was developed to produce a

20 solid concentrate rich in aluminum (precipitated gibbsite), whereas the principal intent of the invented metal-silicate carbonation process is to form stable metal-carbonate compounds for long-term CO_2 sequestration. Due to this key difference, the "ore" used for the two processes is much different. In the Bayer Process, deeply weathered, unconsolidated rock material is reacted because it is rich in alumina and poor in silica.

25 In the present invention, the silica content of the metal-silicate feedstock is not a significant factor, except that a greater silica content generally means a lower Ca, Mg and/or Fe content, which is undesirable. The second key difference is that, in the present invention, caustic soda is regenerated during crystallization of one or more solid metal carbonates, whereas in the Bayer Process, caustic soda is regenerated

30 during the production of high-purity gibbsite.

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In the commercial process of reacting trona with lime (CaO) to produce caustic soda plus calcite, the intent is solely to produce caustic soda; the entire amount of calcite formed as a byproduct is subsequently calcined to regenerate lime, which is recycled for reaction with additional batches of trona ore to produce more caustic soda. Thus, there is no CO_2 sequestration achieved in the commercial treatment of trona. Moreover, trona contains little or no silica and alumina; consequently, its treatment to generate caustic soda does not consume or produce any significant amount of silicate material.

The invented metal-silicate carbonation process may have the following practical uses and benefits:

• CO_2 sequestration. The process was designed mainly to produce crystalline carbonates that persist indefinitely in most continental settings. The results of autoclave experiments presented in Tables 1 and 2 demonstrate that, under suitable conditions: Ca-rich silicates are readily converted to calcite ($CaCO_3$) ± carbonate-cancrinite [$Na_8(AlSiO_4)_6CO_3 \cdot 2H_2O$], and Mg-rich silicates are quickly transformed to magnesite ($MgCO_3$) and/or eitelite [$Na_2Mg(CO_3)_2$]. These four crystalline carbonate compounds bind CO_2 indefinitely in most non-acidic terrestrial environments, and are completely harmless to all flora and fauna.

• Neutralization of highly acidic soils. Locally, calcium and magnesium carbonates can have commercial value as soil amendments. While adding carbonates to highly acid soils to increase pH ultimately releases CO_2 to the atmosphere, significant environmental and economic benefits would accrue if the treated land was made more biologically productive. The amended soils might be used to grow crops or trees, either of which could have a total carbon sequestration potential higher than that of the crystalline carbonate amendment. Using calcium and magnesium carbonates for this purpose would also lessen demand for lime produced by calcining limestone, and this would help lower CO_2 emissions to the atmosphere.

• Recovery of useful metals. Many rock formations contain useful metals (e.g., iron, copper, nickel and platinum) at concentrations that are currently uneconomical to mine. If, however, mining and grinding were already being performed to create a

21

metal-silicate feedstock for carbonation, one or more metals that are not carbonated could be extracted as a byproduct(s), thereby reducing the costs of metal-silicate carbonation.

- Elimination of hazardous mine tailings. Mine tailings, consisting of crushed rock material from which metals or other valuable materials have been extracted—along with the "overburden" (soil and regolith) that is removed to access buried ore horizons—are an important waste problem for many active and abandoned mines. Thus, it is significant that a nearby mineral carbonation reactor might be able to use them as a source of calcium and magnesium. This would enhance environmental restoration, and reduce the costs of mining metal silicate(s) for carbonation.

- Production of high-purity silica. When olivine and/or serpentine is (are) carbonated by the invented process, the solid effluent produced in step 2 (Reactions 12 and 15) is high-purity silica, which can be refined for use in manufacturing silica-based desiccants, silica brick, silicon carbide, and various types of glass. High-purity silica is also a potential source of elemental silicon—the foundation material for numerous semiconducting electronic devices. Finally, it may be possible to use amorphous silica to form melanophlogite, a silica-rich compound with a cage structure that can accommodate as many as six CO_2 "guest" molecules for every 46 molecules of SiO_2. Creation of substantial amounts of melanophlogite would significantly increase the total CO_2-loading of the solids generated by the invented process.

- Production of high-purity magnesite. When olivine and/or serpentine is (are) carbonated by the invented process, the solid effluent produced in step 3 for olivine carbonation (Reaction 13) and in steps 3 and 4 for serpentine carbonation (Reactions 16 and 17) is high-purity magnesite, which can be used to produce magnesite cement.

- Capture and separation of CO_2 from flue gas. Another potential application of the invented process is especially important, as it would greatly reduce costs associated with capture and separation of CO_2 at fossil fuel-fired power plants, cement factories, and steel mills. Specifically, step 2 in the process (e.g., Reactions 6, 9, 12 and 15) permits CO_2 to be captured and separated from flue gas by bubbling the gas

22

through a NaOH- and/or Na_2SiO_3-bearing aqueous liquid. The CO_2 would be transformed to aqueous ± crystalline Na_2CO_3 and/or $NaHCO_3$, and the nitrogen-rich gas effluent could either be refined to produce high-purity nitrogen for commercial use, or simply released harmlessly to the atmosphere.

Table 1. Results of Experiments with Solid Calcium Silicates

Date/ Duration[@]	Starting Materials[@,#]	Temperature/ Pressure	XRD Number	Solid Run Products, and Initial/Final Solution pH[&]
7-10-02/ 72 hrs	anorthite + NaOH + H_2O	200°C/ <15 atm	LMAS001-2 LMAS003	portlandite + hydroxy-sodalite + hydrogrossularite(?)
8-1-02/ 72 hrs	anorthite + NaOH + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA059	calcite + hydroxy-sodalite
10-4-02/ 72 hrs	prereacted anorthite + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA070	calcite + carbonate-cancrinite, pH: 12.5/≥14
8-20-02/ 72 hrs	labradorite + NaOH + H_2O	200°C/ <15 atm	LMA060	portlandite + hydroxy-sodalite + cancrinite + hydrogrossular(?)
8-28-02/ 72 hrs	labradorite + NaOH + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA061	calcite + hydroxy-sodalite + hydrogrossular + minor AUCP, pH: 12.5/≥14
10-8-02/ 72 hrs	prereacted labradorite + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA071	calcite + carbonate-cancrinite, pH: 12.5/≥14
11-8-02/ 72 hrs	$Ca(OH)_2$ + $Mg(OH)_2$ + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA077	calcite + brucite, pH: 12.5/≥14
11-26-02/ 72 hrs	wollastonite + NaOH + H_2O	200°C/ <15 atm	LMA081	sodium-calcium hydroxysilicate
12-2-02/ 72 hrs	wollastonite + NaOH + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA083	calcite + sodium-calcium hydroxysilicate, pH: 12.5/≥14
12-10-02/ 72 hrs	Ca-rich fly ash + NaOH + H_2O	200°C/ <15 atm	LMA084	sodalite + AUCP
12-13-02/ 72 hrs	Ca-rich fly ash + NaOH + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA085	calcite + carbonate-cancrinite + sodalite + AUCP, pH: 12.5/≥14
12-17-02/ 72 hrs	$Ca(OH)_2$ + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA089	calcite, pH: 12.5/≥14
1-3-03/ 72 hrs	prereacted wollastonite + NaOH + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA094	calcite + pectolite, pH: 12.5/≥14
9-16-02/ 72 hrs	basalt + NaOH + H_2O	200°C/ <15 atm	LMA064	portlandite + sodalite + brucite

24

Table 1. Results of Experiments with Solid Calcium Silicates (Cont'd)

Date/ Duration[@]	Starting Materials[@,#]	Temperature/ Pressure	XRD Number	Solid Run Products, and Initial/Final Solution pH[&]
9-30-02/ 72 hrs	basalt + NaOH + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA063	brucite + AUCP
10-14-02/ 72 hrs	prereacted basalt + NaOH + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA059	calcite + carbonate-cancrinite, pH: 12.5/≥14

[@]Sources of solid-silicate starting materials: wollastonite—Willsboro, NY; anorthite—Grass Valley, CA; labradorite—Nain, Labrador, Canada; basalt (USGS standard BCR-2)—Portland, OR; Ca-rich fly ash, Joseph City, AZ; $Ca(OH)_2$ (portlandite)—commercially manufactured, reagent-grade chemical compound; $Mg(OH)_2$ (brucite)—commercially manufactured, reagent-grade chemical compound. NaOH (caustic soda) was added to each unreacted starting sample as a 50 weight percent solution of NaOH in H_2O.

#For each solid silicate, "prereacted" means reaction with a 50 weight percent solution of NaOH in H_2O at 200°C, P <15 atm, before the experiment was performed. In all cases, this step had the effect of converting the silicates to crystalline hydroxide(s) prior to reaction with Na_2CO_3 to form one or more crystalline carbonate compounds.

[&]Chemical compositions of crystalline reaction products: calcite—$CaCO_3$; portlandite—$Ca(OH_2)$; hydroxy-sodalite—$Na_8(AlSiO_4)_6(OH)_2$; sodium-calcium hydroxysilicate—$NaCaSiO_3(OH)$; carbonate-cancrinite—$Na_8(AlSiO_4)_6CO_3 \cdot 2H_2O$; brucite—$Mg(OH)_2$; pectolite—$NaCa_2Si_3O_8(OH)$; hydrogrossular—$Ca_3Al_2(SiO_4)_3 \cdot xH_2O$. AUCP = additional unidentified crystalline phase(s).

Table 2. Results of Experiments with Crystalline Magnesium Silicates

Date/ Duration@	Starting Materials@,#	Temperature/ Pressure	XRD Number	Solid Run Products, and Initial/Final Solution pH&
6-10-02/ 72 hrs	serpentine + NaOH + H_2O	200°C/ <15 atm	LMAS001-1	brucite + relict serpentine
7-1-02/ 72 hrs	olivine + NaOH + H_2O	200°C/ <15 atm	-	brucite
7-16-02/ 72 hrs	prereacted olivine + Na_2CO_3 + H_2O	200°C/ <15 atm	LMAS006	brucite
9-20-02/ 24 hrs	serpentine + NaOH + H_2O	200°C/ <15 atm	LMA069	brucite + trace AUCP
9-23-02/ 72 hrs	serpentine + NaOH + H_2O	200°C/ <15 atm	LMA067	brucite + trace AUCP
9-25-02/ 72 hrs	$Mg(OH)_2$ + Na_2CO_3 + H_2O	200°C/ <15 atm	LMA072	brucite, pH: 12.5/12.5
10-17-02/ 72 hrs	serpentine + NaOH + H_2O	22°C/ 1 atm	LMA073	serpentine + brucite
10-18-02/ 72 hrs at 22°C, then 3 hrs at 200°C	serpentine + NaOH + H_2O	22°C/ 1 atm, 200°C/ <15 atm	LMA075	brucite + minor relict serpentine
11-15-02/ 72 hrs	$Mg(OH)_2$ + Na_2CO_3 + H_2O	300°C/ <86 atm	LMA078	brucite
11-19-02/ ~1 hr	$Mg(OH)_2$ + Na_2CO_3 + H_2O	375°C/ <220 atm	LMA079	brucite
12-23-02/ 72 hrs	$Mg(OH)_2$ + Na_2CO_3 + H_2O	200°C/ ~60 atm*	LMA088	eitelite + minor relict brucite
12-30-02/ 72 hrs	$Mg(OH)_2$ + H_2O	200°C/ ~60 atm*	LMA090	magnesite + minor relict brucite, final pH: 5.5
1-17-03/ 72 hrs	$Mg(OH)_2$ + Na_2CO_3 + H_2O	300°C/ ~60 atm*	LMAS014	brucite + eitelite, pH: 11.5-12/12
3-17-03/ 72 hrs	$Mg(OH)_2$ + Na_2CO_3 + H_2O	100°C/ <1 atm	LMAS017	brucite + magnesium carbonate hydrate

Table 2. Results of Experiments with Crystalline Magnesium Silicates (Cont'd)

Date/ Duration[@]	Starting Materials[@,#]	Temperature/ Pressure	XRD Number	Solid Run Products, and Initial/Final Solution pH[&]
3-21-03/ 72 hrs	$Mg(OH)_2$ + Na_2CO_3 + H_2O	80°C/ <1 atm	LMAS022	brucite + magnesium carbonate hydrate, pH: 12.5/12.5
4-07-03/ 72 hrs	$Mg(OH)_2$ + Na_2CO_3 + H_2O	125°C/ <2 atm	LMAS030	brucite + magnesium carbonate hydrate , final pH: 11.5
4-16-03/ 72 hrs	$Mg(OH)_2$ + $NaHCO_3$ + H_2O	200°C/ <15 atm	-	magnesite + minor eitelite + minor relict brucite

[@]Sources of crystalline silicate starting materials: olivine—Twin Sisters Peak, WA; serpentine (antigorite variety)—Cedar Hill Quarry, Lancaster County, PA; $Mg(OH)_2$ (brucite)—commercially manufactured, reagent-grade chemical compound. NaOH (caustic soda) was added to each unreacted starting sample as a 50 weight percent solution of NaOH in H_2O.

#For each solid silicate, "prereacted" means reaction with a 50 weight percent solution of NaOH in H_2O at 200°C, P <15 atm, before the experiment was performed. In all cases, this step had the effect of converting olivine or serpentine to brucite prior to reaction with Na_2CO_3 or $NaHCO_3$ to form one or more crystalline carbonate compounds.

*A total (fluid) pressure of approximately 60 atm was achieved by injecting CO_2 into the headspace of the autoclave, and keeping that space connected to an external cylinder filled with liquid CO_2 at room temperature.

[&]Chemical compositions of crystalline reaction products: olivine—Mg_2SiO_4; serpentine— $Mg_3Si_2O_5(OH)_4$; brucite—$Mg(OH)_2$; eitelite—$Na_2Mg(CO_3)_2$. magnesium carbonate hydrate—$MgCO_3 \cdot xH_2O$. AUCP = additional unidentified crystalline phase(s).

In accordance with the provisions of the patent statutes, the principle and mode of operation of this invention have been explained and illustrated in its preferred embodiments. However, it must be understood that this invention may be practiced otherwise than as specifically explained without departing from its spirit or scope.